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## Chemical modifications and applications of alternating aliphatic polyketones

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## Chapter 2

# Polymeric amines by chemical modifications of alternating aliphatic polyketones

### Abstract

Alternating aliphatic polyketones were chemically modified using di-amines to obtain polymeric products having pendant amino groups. The used Paal-Knorr reaction involves the formation of pyrrole rings along the polyketone backbone. The corresponding kinetics and final conversions are clearly dependent, among others, on statistical factors (two adjacent carbonyls must react in order to obtain ring formation) as well as on the steric hindrance (sterically hindered amino groups react very slowly). The corresponding reaction products (polymeric amines) display very interesting physical properties in aqueous solution such as formation of micelles at low protonation level, polyelectrolyte behaviour at high protonation level. These properties have been characterized by using dynamic light scattering, Cryo-electron microscopy, and drop tensiometry.

**Key word:** Chemical modifications; Polymeric amines; Polymeric surfactants; Paal-Knorr

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## 2.1 Introduction

The synthesis of polymers containing amine groups has stimulated an enhanced interest in recent years due to their wide applications as emulsifiers, drug carriers, DNA-carriers for gene delivery, cation-exchange resins, and pharmaceutical uses.<sup>1-4</sup> However, the high reactivity of the amine groups due to their inherent ability to act as bases, reducing agents, nucleophiles or as ligands for transition metals, make the preparation of this kind of polymers quite difficult and problematic.<sup>5</sup> Alternating polyketones can act as precursors for the preparation of polymeric amines (polyamines) by chemical modifications via the classic Paal-Knorr reaction, in which the 1,4-di-carbonyl moiety of the polyketones reacts with a primary amine function yielding a pyrrole unit. In contrast to a variety of polymerization mechanisms such as anionic, cationic or radical ones, the route of chemical modifications of polyketones described here just consists of a two components/one-pot reaction without the need of any catalysts and organic solvent using mild conditions during the whole process. It represents a simple, low cost, and straightforward way to prepare the polyamines.

In the present work, we report the synthesis of a family of polyamines by chemical modifications of alternating aliphatic polyketones with a set of functional di-amines via the Paal-Knorr reaction. The resulting polyamines possess double functionalities: the N-substituted 2,5-pyrrole-diyl group incorporated in the polymer backbone and a substituent containing an amino functionality which can be either primary, secondary or tertiary and both aliphatic or aromatic. The factors affecting the chemical reactivity of the polyketones with the di-amines such as reaction conditions (time, temperature, and initial molar ratio between amino groups of the di-amines and 1,4 arrangement of di-carbonyl groups on the polyketones), ethylene content of the polyketones, and chemical structure of the di-amines were thoroughly studied. The polyamines are expected to transform into water-soluble cationic species by simple protonation with weak acid or by quaternization of the amino groups. Thus physical properties of the polyamines as water dispersion were characterized by a combination of dynamic light scattering (DLS), surface tension, and Cryo-transmission electron microscopy (Cryo-TEM). Furthermore, as aromatic rings (pyrroles) are present in the backbone of the polymer, a study of the fluorescence property of the polyamines was carried out in water solution.

## 2.2 Experimental

**Materials.** The alternating polyketones with 0% ethylene (PK0, Mw-1680), 30% ethylene (PK30, Mw-3970) and 50% ethylene (PK50, Mw-5350) based on the total olefin content were synthesized according to a reported procedure.<sup>6-7</sup> 1,2-diaminopropane (1,2-DAP, Acros, 99%), 1,3-diaminopentane (1,3-DAPe, Aldrich, 98%), 2-(Dimethylamino) ethylamine (2-DAEA, Aldrich,  $\geq 98\%$ ), 2-diethylaminoethylamine (2-DEAEA, Aldrich, 95%), 4-Picolylamine (4-PcA, Aldrich,  $\geq 97\%$ ), 2,5-hexanedione (Aldrich,  $\geq 99\%$ ), acetic acid (Acros,  $\geq 99.7\%$ ), methyl iodide (Aldrich, 99%), and tetrahydrofuran (THF, Acros,  $\geq 99\%$ ) were purchased and used as received.

**Model component reaction.** 2,5-hexanedione (0.3 mmol) was added to 1,2-diaminopropane (0.3 mmol) in 0.7 ml of  $\text{CDCl}_3$ . The resulting mixture was shaken for 2 min and transferred into an NMR tube (5 mm in diameter). The progress of the reaction was monitored with  $^1\text{H}$  NMR spectroscopy at 50 °C for 11.25 h. The spectra were recorded at regular time intervals of 25 min.

**Chemical modifications of the polyketones.** The chemical modifications were carried out in a sealed 250 ml round bottom glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. In order to calculate the stoichiometry of the Paal-Knorr reaction, the amount of 1,4-arrangement of di-carbonyl reactive species in 40 g polyketones were first calculated. Here, PK30 was taken as example. The repeating units of CO/propylene and CO/ethylene is  $\text{C}_8\text{H}_{12}\text{O}_2$  with a mol mass of 140 and  $\text{C}_6\text{H}_8\text{O}_2$  with a mol mass of 112, respectively. Thus, the average mol mass of the repeating unit for PK30 is  $(0.7 \times 140) + (0.3 \times 112) = 131.6$ , so that 40 g of PK30 contains  $40/131.6 = 0.3$  mol reactive species. The amount of di-amines (e.g. 1,2-DAP) when used for reaction in equimolar ratio between the di-amines and di-carbonyl groups of the polyketones is  $0.3 \times 74.12$  (Mw of 1,2-DAP) = 22.24 g. After the polyketones (40 g) were preheated to the liquid state at the employed reaction temperature (80-100 °C), the di-amines were added dropwise into the reactor in the first 20 min. The stirring speed was set at a constant value of 500 rpm. During the reaction, the mixture of the reactants changed from the slight yellowish, low viscous state into a highly viscous brown homogeneous paste. The reaction conversion was monitored using potentiometric titrations. After the reactions were completed and the polymers cooled down to room temperature, the products derived from the 1,2-DAP and 4-PcA changed into rigid solid material, while the other products appeared as waxy or soft materials at room temperature. The resulting polyamines were washed several times with de-ionized Milli-Q water to remove unreacted di-amines. After filtering and freeze-drying, light brown polymers were obtained as the final products.

**Preparation of polymer solutions.** The polyamines as such are not soluble in water. However, they display good solubility in acidic water. Accordingly, 100 mg/ml stock solutions of PK30 modified with 1,2-DAP and 1,3-DAPe in de-ionized Milli-Q water were prepared by adding the appropriate amount of acetic acid solution to match a desired protonation level and stirring with a magnetic stir-bar at 80 °C for 1.5 h. The tertiary amino groups of PK50 modified with 2-DAEA, 2-DEAEA, and 4-PcA, and PK30 modified with 4-PcA were quaternized by treating the polymers with a ten molar excess of methyl iodide over the amino groups in THF at room temperature for 24 h. The solvent and excess methyl iodide were removed under reduced pressure. The 10 mg/ml stock solutions of the quaternized polymers were prepared in the de-ionized Milli-Q water by stirring with a magnetic stir-bar at 80 °C for one hour and then passing through 200 nm syringe filters after complete dissolution. All solutions were equilibrated overnight before any further measurements were performed.

**Nuclear magnetic resonance (NMR) and FTIR spectroscopy.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer using  $\text{CDCl}_3$  as a solvent. FTIR spectroscopy was performed on a Perkin-Elmer Spectrum 2000 and spectra of the polymers were recorded by using KBr pellets.

**Potentiometric titrations.** Potentiometric titrations were performed at room temperature for determination of the amine number of the modified polyketones using a titrator (702 SM Titrino, Metrohm) with an automatic burette of 10 ml capacity. A perchloric acid ( $\text{HClO}_4$ , 0.1 M) solution in water, standardized by potassium hydrogen phthalate, was used as the titrating agent. A THF/water (9:1) mixture, which is able to solubilize the polyamines at all protonation levels (i.e. during all the titrations), was used as titration solvent (120 ml) for the samples (0.2-0.3 g). The inflection point was identified from the titration curve. Three or four measurements were performed for each reaction sample. The average amine number was taken and the obtained standard error of the average value was less than 1%. The conversion of the di-amines,  $X_{amine}$ , and carbonyl groups of the polyketones,  $X_{CO}$ , were determined by the following formulas:

$$X_{amine} = (A_i - A_f) / A \times 100\% \quad (1)$$

$$X_{CO} = X_{amine} \times I_{am/CO} \times 100\% \quad (2)$$

where  $A_i$  is the amine number before the modification,  $A_f$  is the amine number after the modification,  $A$  is the standard amine number for 100% conversion value,  $I_{am/CO}$  is the initial reaction molar ratio between the di-amines and 1,4-arrangement of di-carbonyl groups of the polyketones.

**Dynamic light scattering.** The dynamic light scattering (DLS) measurements were performed on a Zetasizer 5000 instrument (Malvern Instruments, UK) at a wavelength of 633 nm and at a temperature of 25 °C. Scattered light was detected at a 90 degree angle. The viscosity (0.89 mPa.s) and the refractive index (1.33) of water at 25°C were used for data analysis. The intensity autocorrelation functions obtained from the DLS were analyzed by using a CONTIN algorithm for all measurements. The apparent hydrodynamic diameter,  $D_H$ , was obtained using the Stokes-Einstein relation:

$$D_0 = kT / 3\pi \eta D_H \quad (3)$$

where  $D_0$  is the diffusion coefficient,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of the solution.

**Drop tensiometry.** Surface tension measurements on the polymer solutions were performed by using a drop tensiometer (Lauda, TVT-1), with a Lauda RM6 temperature controller. The temperature was controlled at 25±0.1 °C during the period of measurements. The inner radius of the steel capillary was 1.055 mm and the employed syringe had a volume of 500 µl. The surface tension value for de-ionized Milli-Q water (70 mN/m) was taken as an internal standard before starting measurements. The error given by the instrument was less than 0.1 mN/m.

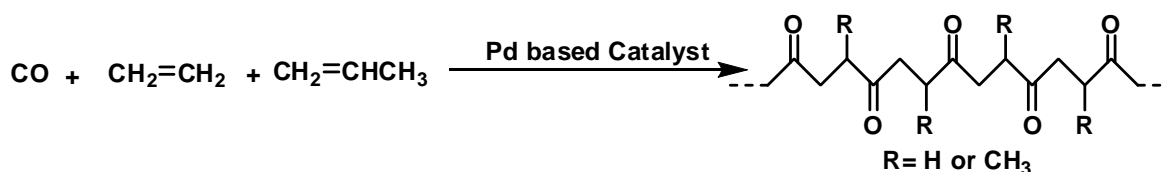
**Cryo-transmission electron microscopy.** A drop of the polymer solution was deposited on a glow discharged carbon-coated grid. After blotting away the excess of solution with filter paper, the grids were rapidly plunged into liquid ethane. The frozen specimen were transferred to a Gatan (model 626) cryo-stage and examined in a Philips CM 120 cryo-electron microscope operating at 120 kV. Micrographs were recorded under low-dose conditions at about -170 °C.

**Fluorescence spectroscopy.** The fluorescence measurements were performed on a Fluorolog 3-22 spectrofluorimeter. The spectra were recorded between 365 nm and 650 nm with the excitation wavelength of 350 nm. The slit width of the emission was kept at 1 nm step size. All the measurements were performed in the de-ionized Milli-Q water at room temperature.

## 2.3 Results and discussion

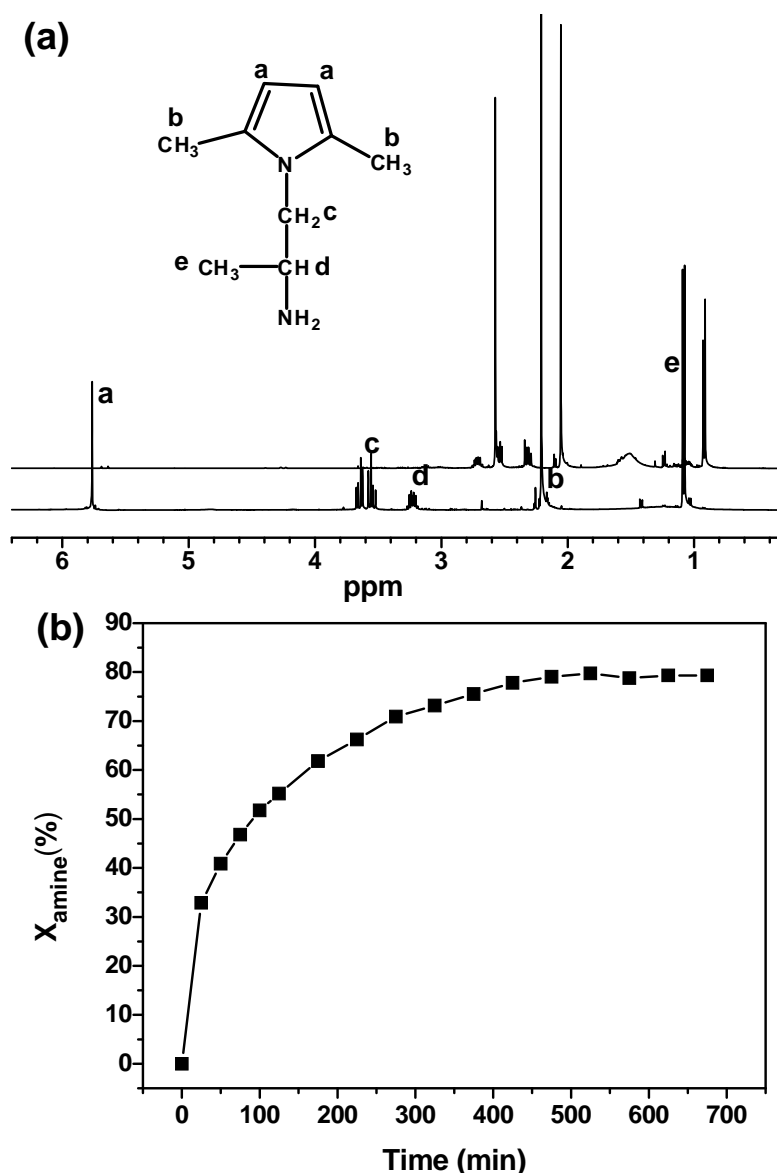
### 2.3.1 Chemical modifications of polyketones

The current study focused on a new class of the polyketones ( $M_w$  1500-5500), i.e. alternating co- and ter-polymers of carbon monoxide, ethylene, and propylene (Figure 2.1), as starting materials for modifications. Depending on the molar ratio of ethylene and propylene, the consistency of this type of polyketones at room temperature varies from viscous flowing materials for ethylene free materials to waxy or melting solids at 50% ethylene based on the total olefin content.



**Figure 2.1** Synthesis of CO-ethylene-propylene based low molecular weight polyketones.

Since the use of polyketones resulted in low resolution spectra due to the polymeric nature of the substrate, we determined the exact chemical structure of the product by using model compounds. In particular, we carried out the reaction between 1,2-DAP and 2,5-hexanedione in an NMR tube in  $\text{CDCl}_3$ . The NMR spectra of the starting reaction mixtures and after 11.25 h reaction time are reported in Figure 2.2a. The appearance of the pyrrole ring absorptions at about 5.7 ppm, the  $-\text{CH}_2-$  groups attached to the pyrrole ring (3.6 ppm), and the  $>\text{CH}-$  in  $\beta$ -position with respect to the pyrrole rings (3.2 ppm) all testify the formation of the reported product. Moreover, from the ratio of peaks at 1 ppm (methyl group of the reacted 1,2-DAP) and at 0.95 ppm (methyl groups of unreacted 1,2-DAP), it is possible to calculate the conversion at a given time (Figure 2.2b). It is clear that the reaction rate at 50 °C is actually slow, reaching a di-amine conversion of 80% in 11.25 h. On the other hand, by comparison of the  $^1\text{H}$ -NMR spectra before and after reaction, it can also be seen that only the less hindered amino group can react with the carbonyl moieties and the other one remains as pendant from the pyrrole ring, which is in agreement with what is reported in previous studies.<sup>8</sup>

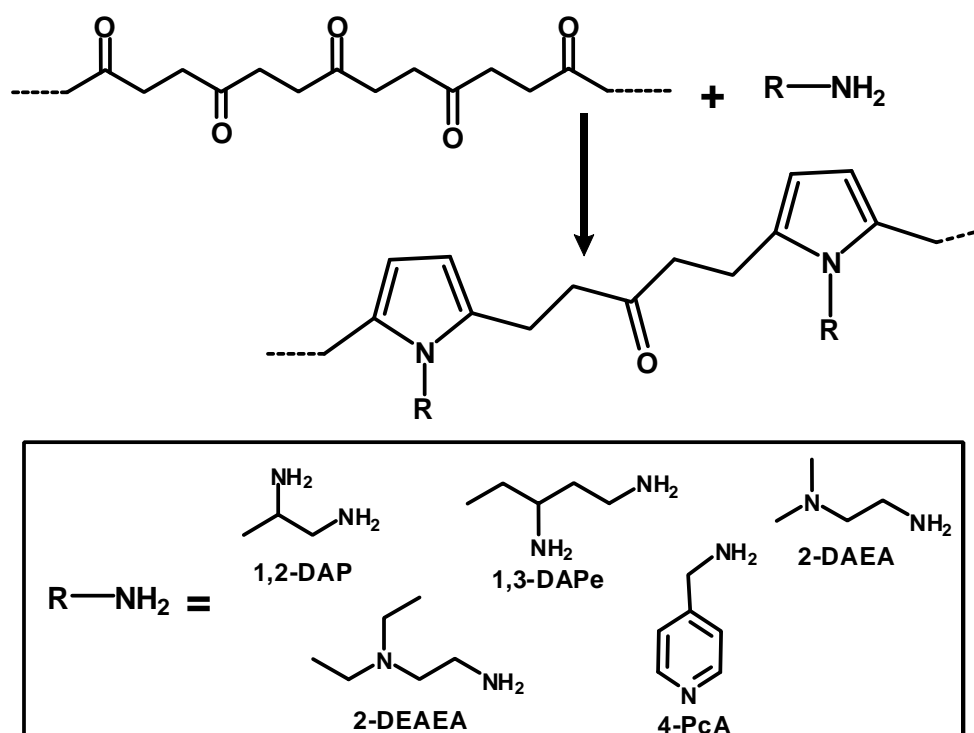


**Figure 2.2** Model compound reactions: (a)  $^1\text{H}$ -NMR spectra before reaction (upper spectrum) and after 11.25 h (lower spectrum); (b) reaction kinetics, determined by  $^1\text{H}$ -NMR.

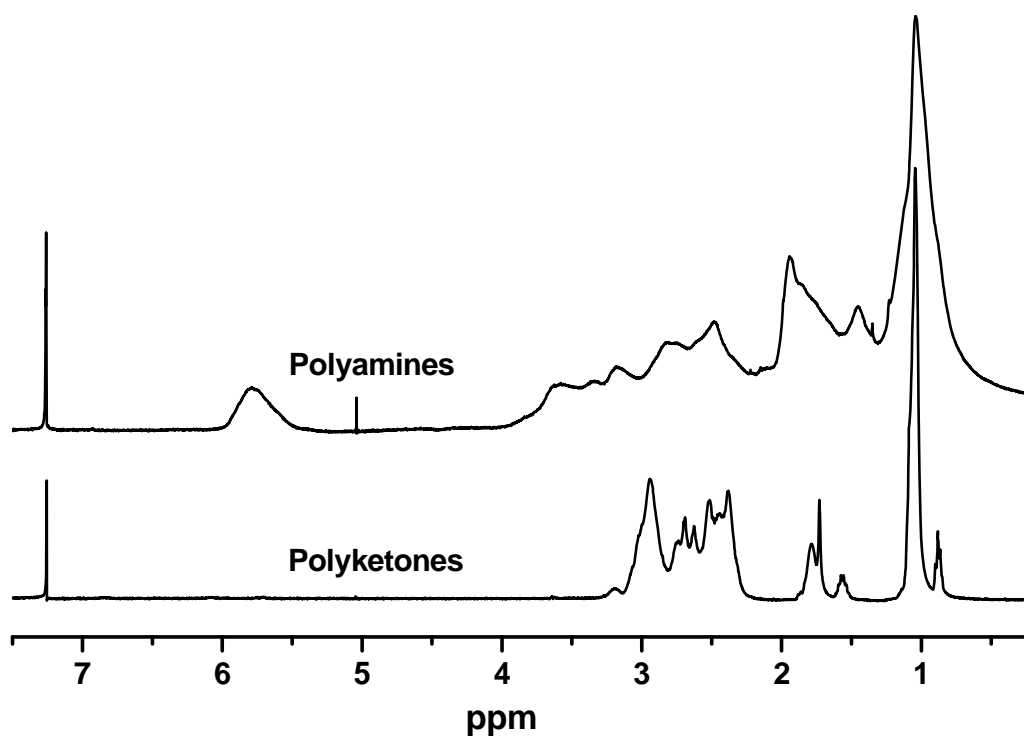
The chemical reactivity of polyketones with different kinds of di-amines has been systematically investigated here (Figure 2.3) by using potentiometric titrations. The mechanism of the Paal-Knorr reaction between a 1,4-di-carbonyl compound and a primary amine involves three steps: addition to the first carbonyl, addition/elimination and rearrangement steps, and stable product formation.<sup>9</sup> The chemical characterization of the final stable product has been well established.<sup>10-15</sup> The presence of pyrrole rings in the backbone of the polyamines has been confirmed by FTIR and NMR analysis on all our reaction products. Typical is the appearance of  $^1\text{H}$ -NMR peaks (Figure 2.4) around 6 ppm (assigned to the protons attached to the pyrrole rings),  $^{13}\text{C}$ -NMR peaks at around 130 ppm



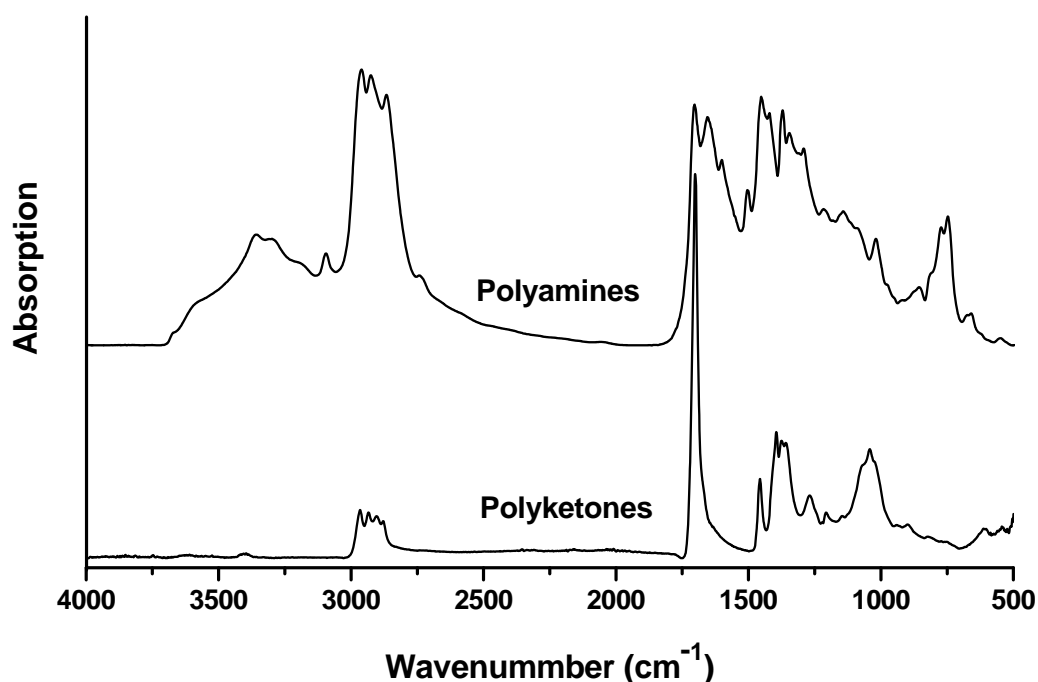
(assigned to the C-atoms of the pyrrole rings), and FTIR absorption peaks (Figure 2.5) at around  $3100\text{ cm}^{-1}$  and  $1500\text{-}1680\text{ cm}^{-1}$  (assigned to the pyrrole rings).



**Figure 2.3** Scheme of the reaction between polyketones and a series of di-amines.

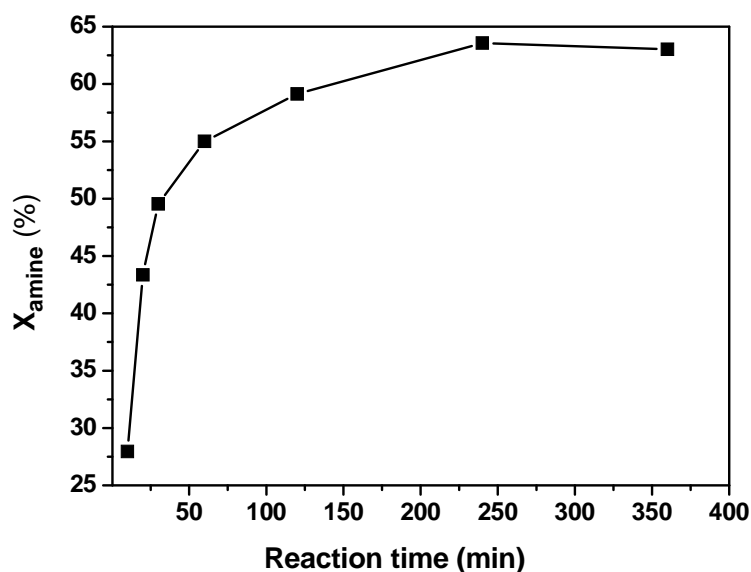


**Figure 2.4** <sup>1</sup>H-NMR spectra of polyketones (PK30) and polyamines (PK30 with 1,2-DAP).



**Figure 2.5** FTIR spectra of polyketones (PK30) and polyamines (PK30 with 1,2-DAP).

A more detailed study for the polymeric systems was set up by carrying out the reactions under different experimental conditions. We first investigated the kinetics of the reaction under mild conditions (50 °C) by determining and calculating the di-amine conversion as function of time (Figure 2.6). An initial molar ratio ( $I_{\text{am/CO}}$ ) of 1 between 1,2-DAP and the 1,4-arrangement of di-carbonyl groups on the PK30 was employed. Due to the steric effect of the 1,2-DAP, only the non-sterically hindered amino group (position 1 in 1,2-DAP) could react with the 1,4-di-carbonyl unit and led to the desired regiospecific reaction. The other one (position 2 in 1,2-DAP) remained intact as functional group. This is consistent with the results of the model component reactions between 2,5-hexanedione and di-amines with steric hindrance<sup>8</sup> and to the data reported above. It can be observed that the conversion increases with the reaction time and reaches a steady value of about 65 % after about 4 h reaction time. The fact that not all amino groups are actually consumed in the reaction (i.e. conversion never reaches 100% for an initial equimolar ratio), is easy to understand if one considers that every amino groups must react with two adjacent carbonyl groups to yield the final pyrrole. Statistically, however, there exists always the chance that two different amino groups will react and result, after ring closure, in two pyrroles separated by a single carbonyl group. In this case, further reaction of the isolated carbonyl-group with another amino group is not possible, thus preventing the amine conversion to reach 100% for an initial equimolar ratio.



**Figure 2.6** Di-amine conversion as a function of time in the reaction of PK30 with 1,2-DAP.

The situation changes when using a different  $I_{\text{am/CO}}$  (Table 2.1) at 80°C after 240 min of reaction time. The di-amine conversion steadily decreases with the amount of the same reactant present originally in the reaction mixture. Moreover, di-amine conversions very close to 100% are observed when using an  $I_{\text{am/CO}}$  of about 0.6 or 0.7. The latter clearly confirms that the limitation in the conversion is not due to the amine reactivity but to the statistical restraint mentioned above. Moreover, from a practical point of view, the same fact indicates that a maximum of about 70% of the carbonyl groups can actually react with the amino groups due to the availability of the 1,4-di-carbonyl groups. The reaction temperature has very little impact on the conversion between 80°C and 100°C (Table 2.2), at least if compared to the influence of the composition. Between 80°C and 100°C the di-amine and carbonyl conversion remains basically unaffected at  $I_{\text{am/CO}}=0.6$  while it increases slightly at  $I_{\text{am/CO}}=0.8$ . These data indicate once more that there is a maximum to the amine amount able to react with the PK30. At the same time the conversion might be improved by increasing the reaction temperature when working in excess of di-amines with respect to the 70 % of carbonyl groups as mentioned earlier.

| $I_{\text{am/CO}}$ | X <sub>amine</sub><br>(%) | X <sub>CO</sub><br>(%) |
|--------------------|---------------------------|------------------------|
| 0.6                | 99                        | 59                     |
| 0.7                | 92                        | 64                     |
| 0.8                | 83                        | 67                     |

**Table 2.1** Conversion of di-amines and carbonyl groups in the reaction of PK30 with 1,2-DAP as a function of  $I_{\text{am/CO}}$  at 80 °C.

| $I_{\text{am/CO}}$ | T<br>(°C) | $X_{\text{amine}}$<br>(%) | $X_{\text{CO}}$<br>(%) |
|--------------------|-----------|---------------------------|------------------------|
| 0.6                | 80        | 99                        | 59                     |
| 0.6                | 100       | 99                        | 59                     |
| 0.8                | 80        | 83                        | 67                     |
| 0.8                | 100       | 90                        | 72                     |

**Table 2.2** Conversion of 1,2-DAP and carbonyl groups as functions of temperature and  $I_{\text{am/CO}}$  for the reaction with PK30.

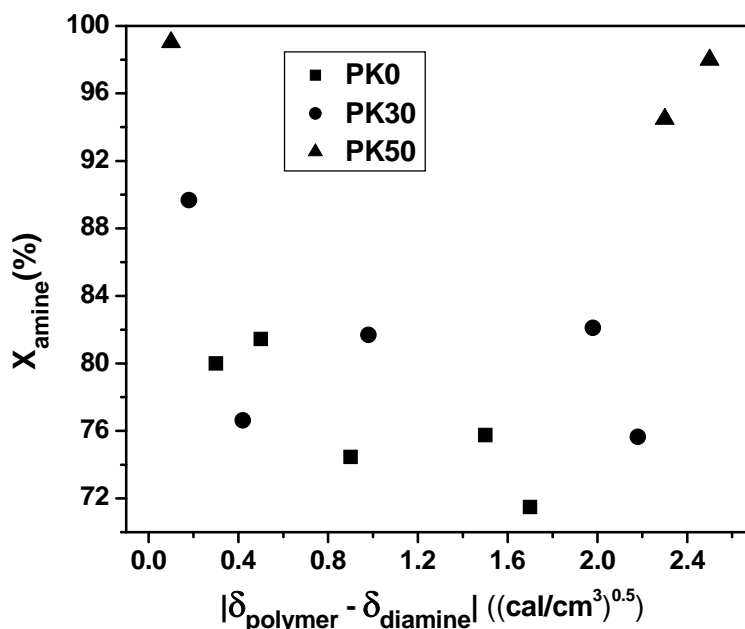
We finally investigated the effect of the chemical structure of the di-amines and the polyketones on the conversion (Table 2.3). All the reactions proceeded exceedingly well except for the unexpected cross-linking of PK50 with 1,2-DAP and 1,3-DAPe. No cross-linking can occur for the PK50 with 2-DAEA, 2-DEAEA, and 4-PcA due to the fact that only primary amino groups are reactive in the Paal-Knorr reaction.

| Di-amines | PK0                    |                     | PK30                   |                     | PK50                   |                     |
|-----------|------------------------|---------------------|------------------------|---------------------|------------------------|---------------------|
|           | $X_{\text{amine}}$ (%) | $X_{\text{CO}}$ (%) | $X_{\text{amine}}$ (%) | $X_{\text{CO}}$ (%) | $X_{\text{amine}}$ (%) | $X_{\text{CO}}$ (%) |
| 1,2-DAP   | 80                     | 64                  | 90                     | 72                  | Cross-linking          |                     |
| 1,3-DAPe  | 81                     | 65                  | 82                     | 65                  | Cross-linking          |                     |
| 2-DAEA    | 76                     | 61                  | 82                     | 66                  | 94                     | 76                  |
| 2-DEAEA   | 71                     | 57                  | 76                     | 61                  | 98                     | 78                  |
| 4-PcA     | 74                     | 60                  | 77                     | 61                  | 99                     | 79                  |

**Table 2.3** Conversion of di-amines and carbonyl groups as functions of the kind of polyketones and di-amines ( $I_{\text{am/CO}}=0.8$ ,  $T=100$  °C,  $t=240$  min).

Due to the steric hindrance, only one amino group of 1,3-DAPe could react with PK0 and PK30, a very similar effect to the one of the 1,2-DAP. The conversion of different di-amines are found to be quite comparable to each other. All the resulting polyamines can be readily dissolved into common organic solvents, such as methanol, ethanol, THF, and chloroform. In contrast, virgin polyketone oligomers (before modifications) are only slightly soluble in protic solvents such as methanol and ethanol. Conversion increases with increasing ethylene content of the polyketones, in particular this leads for 1,2-DAP and 1,3-DAPe to cross-linking when using PK50. It is interesting to note that the di-amine conversion with PK50 can even reach almost 100%, which corresponds to around 80% carbonyl group consumption. This trend could be due either to a different solubility of the different di-amines in the molten polyketones or to the higher reactivity at high ethylene content because of the lower steric hindrance of the carbonyl groups of PK50. However, a

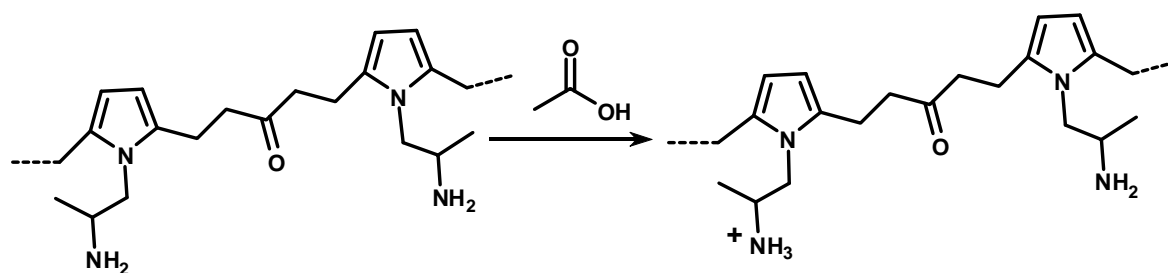
closer look at the value of the solubility parameters<sup>16</sup> for every possible couple of polyketones and di-amines shows that there is no real correlation between solubility (estimated as absolute value of the solubility parameter difference) and di-amine conversion (Figure 2.7). As a consequence, like already stated in the literature<sup>10-11</sup>, we can conclude that the steric effect in the polyketone backbone plays here a major role.



**Figure 2.7** Effect of the difference of solubility parameters between the polyketones and di-amines on the conversion of the di-amines.

### 2.3.2 Characterization of the polymeric amines

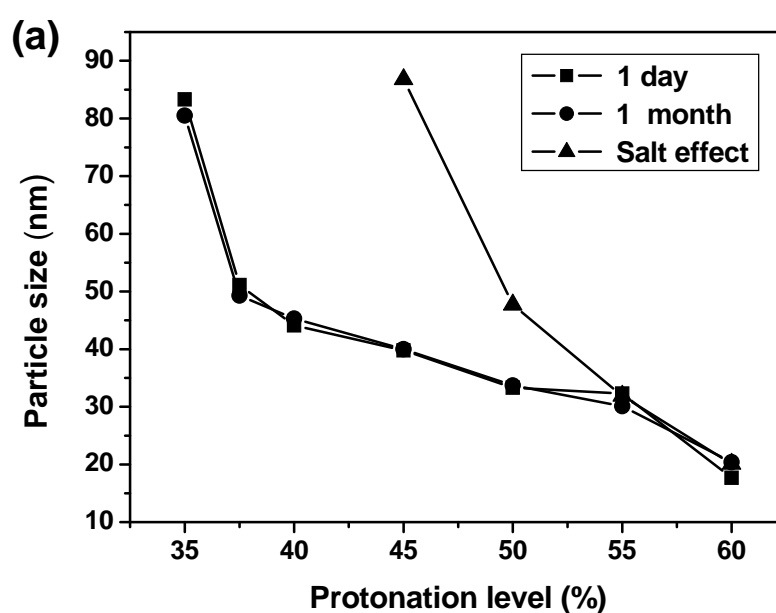
The synthesized polyamines were protonated with the use of acetic acid (Figure 2.8) and successively dispersed in water. They exhibit many interesting physical properties in aqueous solution.

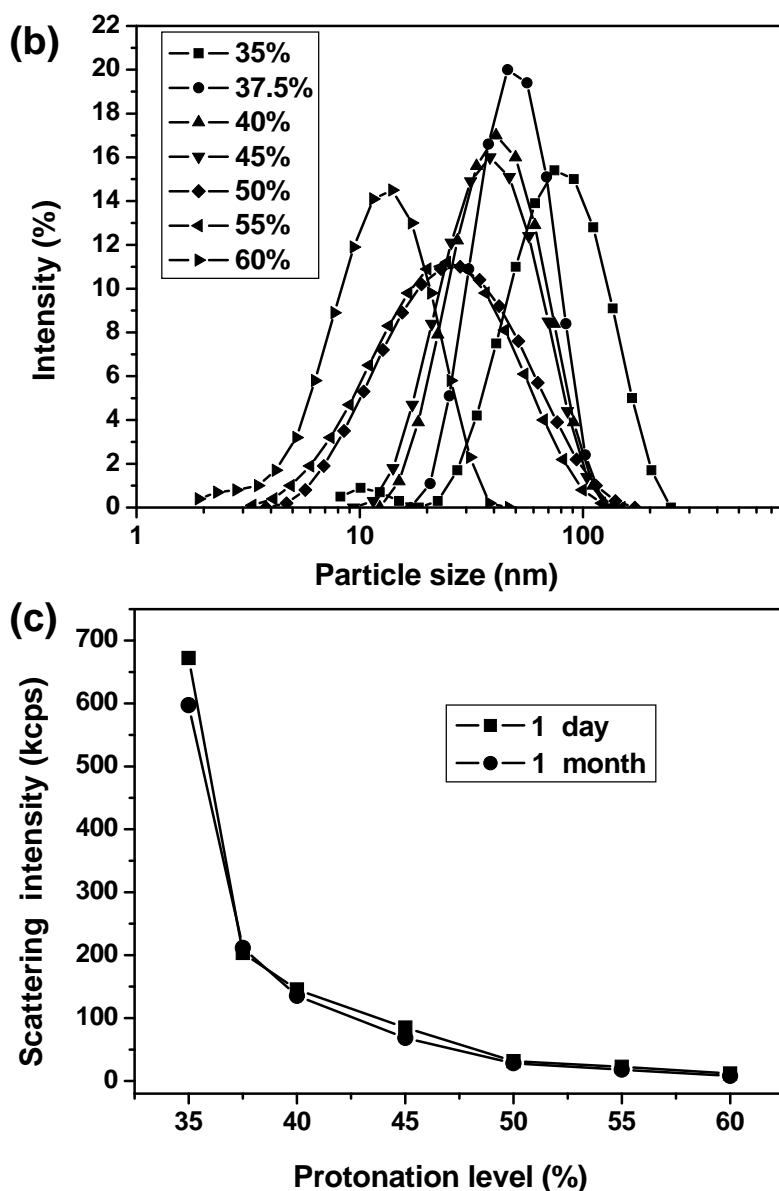


**Figure 2.8** Protonation of polyamines with acetic acid (only derivatives of 1,2-DAP is shown for brevity).

We first investigated the influence of the protonation level on the particle dimension of the resulting dispersion of PK30 modified with 1,2-DAP (Figure 2.9a). Below 35% protonation level, the polymer is insoluble in water and precipitates. In first instance, it must be noticed that the particle size decreases quite significantly with the protonation level. This is most probably related to the stabilization effect which prevents coagulation, due to the positive charges at the interface between the particles and water according to the well-established DLVO theory<sup>17</sup>. A confirmation of this hypothesis is given by the observed salt effect. The addition of NaCl (150 mM) to the dispersion results in a screening of the electrostatic repulsion between particles and therefore leads to an increased average particle size. The salt effect is rather pronounced at low protonation level. Within the protonation level range from 35% to 45%, the addition of the salt leads to the flocculation (salted out) of the polyamines in the solution.

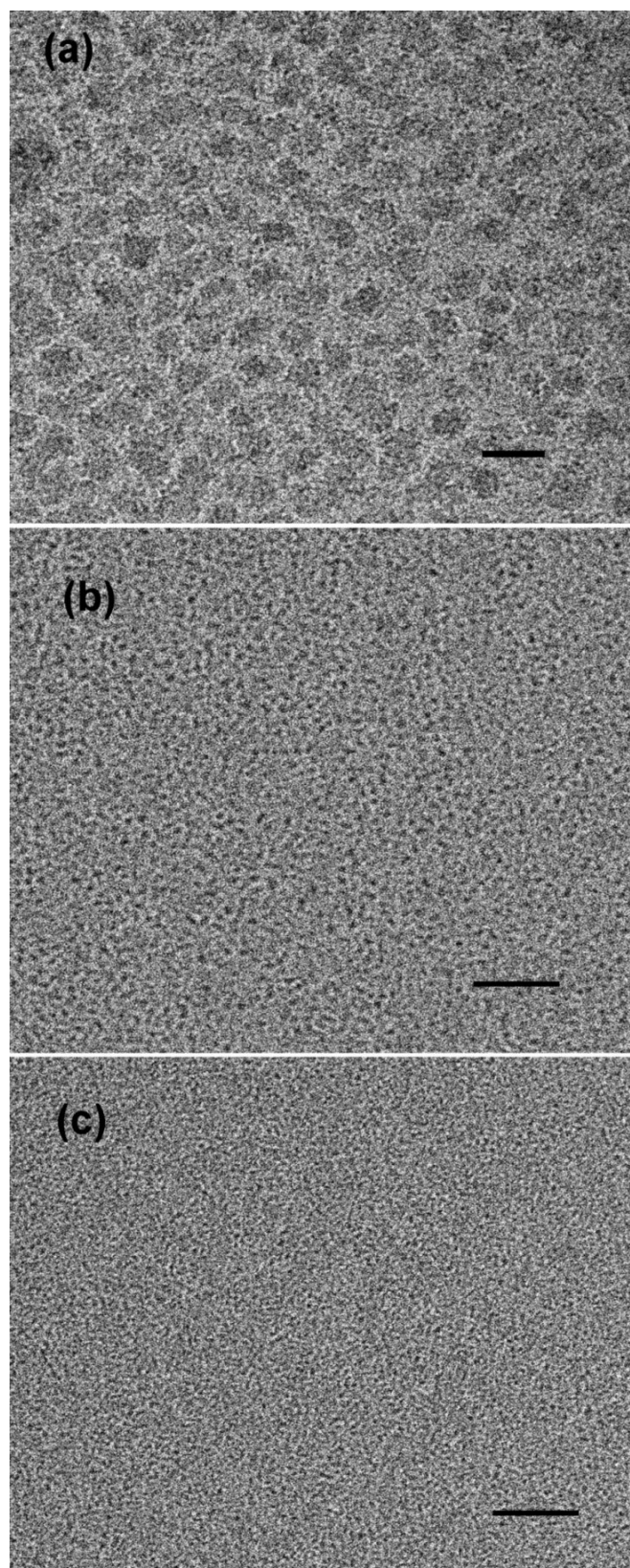
The protonation level affects the particle size but has no remarkable influence on the width of the distribution (Figure 2.9b), which remains basically monomodal at all protonation levels. Moreover, the repulsive electrostatic interaction is strong enough to stabilize the corresponding dispersion even after 1 month storage (Figure 2.9a) at room temperature. The same lack of effect is observed when comparing the scattering intensity, which corresponds to the number of the particles in the solution, as functions of protonation level and time (Figure 2.9c). The increase of the protonation level makes the polymers more hydrophilic and keen to molecularly dissolve into water, thus leading to a decrease of the scattering intensity. A very weak scattering intensity can be observed with further increasing the protonation level above 60%, indicating that the polymers are able to behave like polyelectrolytes and become water soluble.





**Figure 2.9** Influence of protonation level on (a) particle size; (b) particle size distribution; (c) scattering intensity for PK30 modified with 1,2-DAP in water (5 mg/ml).

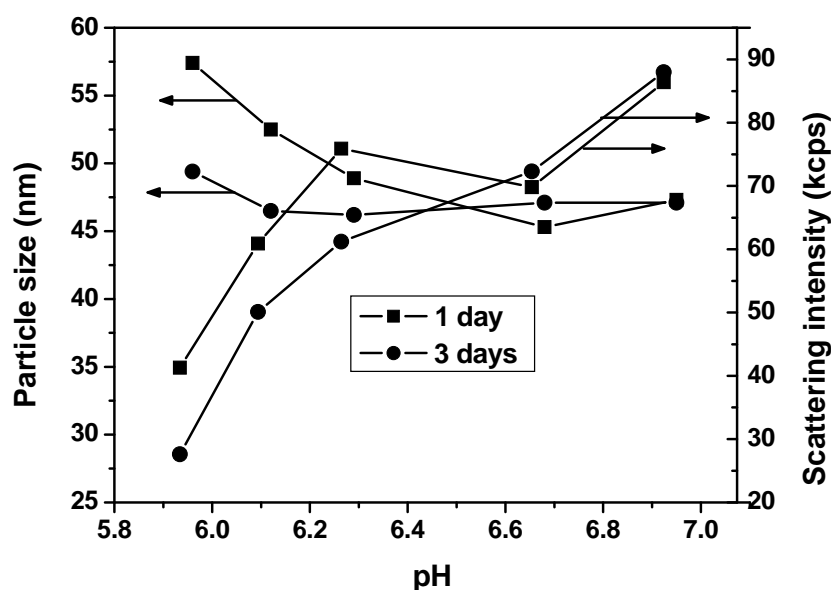
A deeper insight into the particle size and, in general, the morphology of the dispersions was obtained by using Cryo-TEM (Figure 2.10). It is clear how the average particle size decreases with the protonation level, in striking agreement, also from a quantitative point of view, with the light scattering measurements. In this respect, such dispersions could rightly be called “nano”, starting with average dimensions of about 50 nm for the spherical polymer micelles at 40% protonation level and ending up with an average of even less than 10 nm at 100% protonation level. Such outstanding uniformity of the dispersions as well as their stability with respect to time has clear advantages for many practical applications.



**Figure 2.10** Cryo-TEM images of PK30 modified with 1,2-DAP dispersed in water at (a) 40% protonation level; (b) 60% protonation level; (c) 100% protonation level. Bar represents 50 nm.

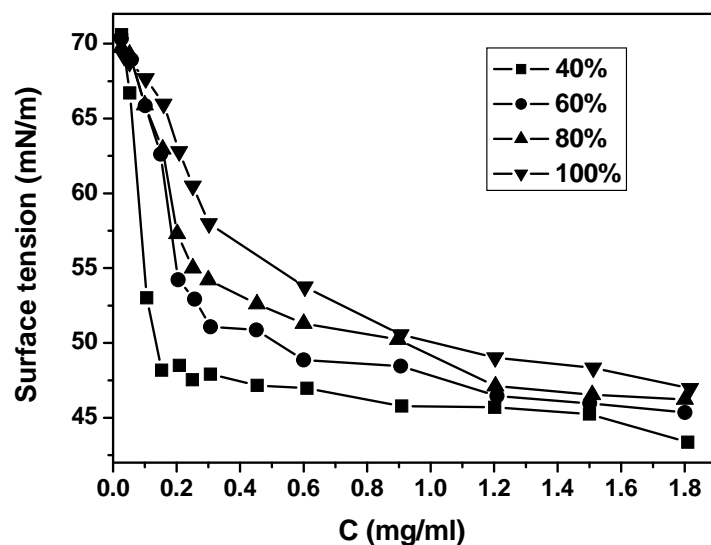


One factor that may remarkably affect both particle size and the light scattering intensity of the dispersions is the sudden pH drop caused by the addition of the strong acid (0.5 M HCl) to polyamine dispersions (Figure 2.11), which may provide useful information for further application as drug carriers<sup>18</sup>. For a derivative of PK30 with 1,2-DAP at 40% protonation level, it is found that once the micelles are formed, the micelle size does not strongly depend on the pH drop even after 1 day and 3 days time-period. However the considerable decrease of the scattering intensity indicates very fast kinetics for the conversion of micelles into unimers, corresponding to deeply protonation of amino groups, once the pH drop is made.



**Figure 2.11** Influence of pH on the particle size and scattering intensity of PK30 modified with 1,2-DAP (2 mg/ml).

The fact that the modified PK30 has a surfactant-like structure or amphiphilic character is not only testified by its chemical structure but also by the measurement of surface tension of the resulting dispersions as functions of the concentration and protonation level of the polyamines (Figure 2.12). Surface tension, indicating the adsorption of the surfactants at the air-water interface, decreases as expected with the concentration of the polyamines and with the protonation level. The latter effect is probably related to the more hydrophobic nature of the modified PK30 with decreasing protonation level, which thus determines its surface activity. This phenomenon is similar to other synthetic block copolymers with a hydrophilic-hydrophobic balance.<sup>19</sup> Surface tension measurements result in a relatively smooth curve due to molecular weight distributions of the polymers, which is a clear difference with that of low molecular weight surfactants. As a result, no well-defined critical micelle concentration (CMC) could be identified.<sup>20</sup>

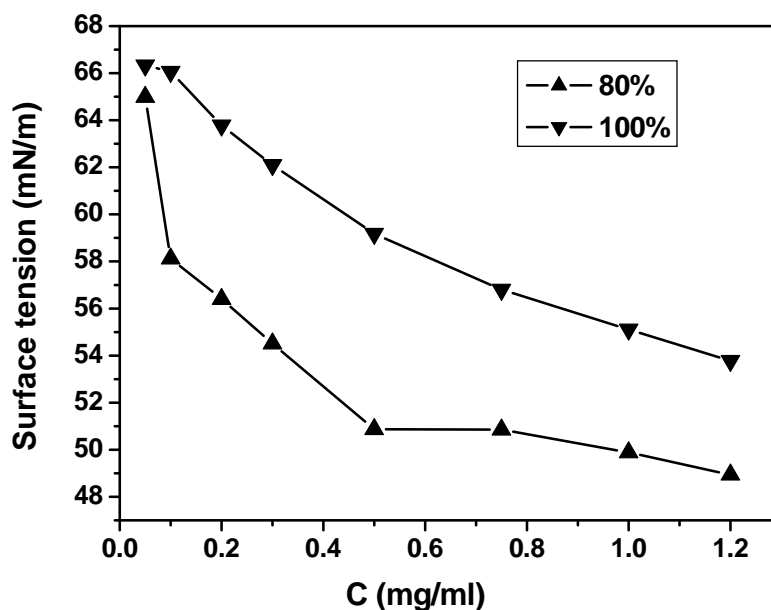


**Figure 2.12** Surface tension of PK30 modified with 1,2-DAP as functions of protonation level and concentration.

Aqueous properties were also studied on the PK30 with 1,3-DAPe (Table 2.4 and Figure 2.13) at two different protonation levels. A very similar aqueous behavior to the one displayed by PK30 modified with 1,2-DAP can be observed. Partial protonation of the amine groups on the PK30 with 1,3-DAPe induces larger, loose aggregates with an average particle size around 300 nm, compared to an average particle size of less than 50 nm for PK30 with 1,2-DAP. This may be correlated with the difference in chemical structure of the used di-amines for modifications, which thus leads to the diversity of the aqueous properties. The polymer solutions display good stability during the 2 weeks of measurement time. The salt effect (150 mM NaCl) here is not as much pronounced as for PK30 with 1,2-DAP. In terms of surface activity, it can be seen in Figure 2.13 that the surface tension decreases with an increase in the concentration and, as expected, low protonation levels result in a higher surface activity.

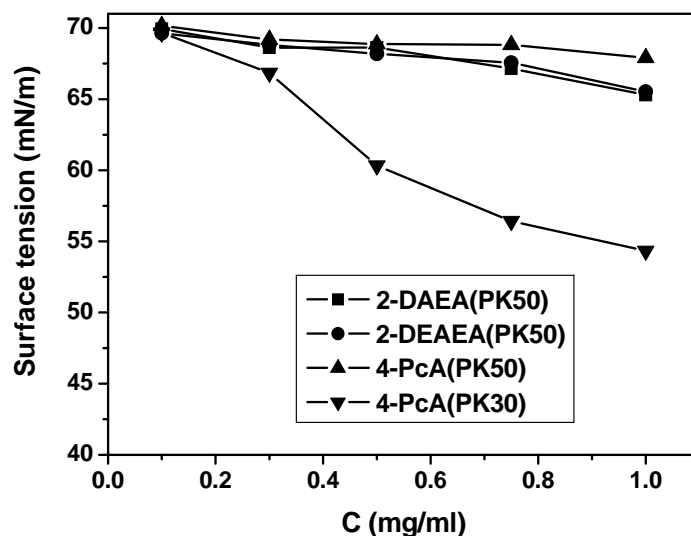
| Protonation level (%) | Particle size (nm) | Scattering intensity (kcps) |
|-----------------------|--------------------|-----------------------------|
| 70 (1 day)            | 302                | 425                         |
| 70 (2 weeks)          | 295                | 350                         |
| 70 (salt effect)      | 264                | 410                         |
| 80 (1 day)            | 296                | 163                         |
| 80 (2 weeks)          | 265                | 190                         |
| 80 (salt effect)      | 263                | 176                         |

**Table 2.4.** Influence of the protonation level on the particle size and scattering intensity of PK30 modified with 1,3-DAPe.



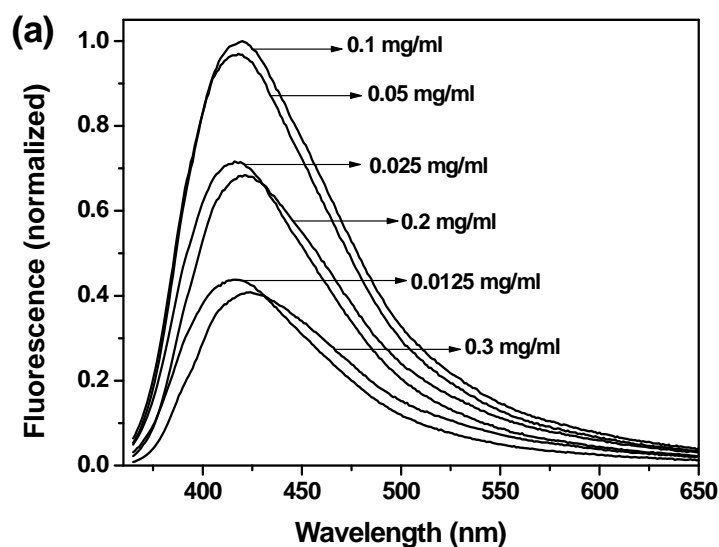
**Figure 2.13** Surface tension of PK30 modified with 1,3-DAPE as functions of protonation level and concentration.

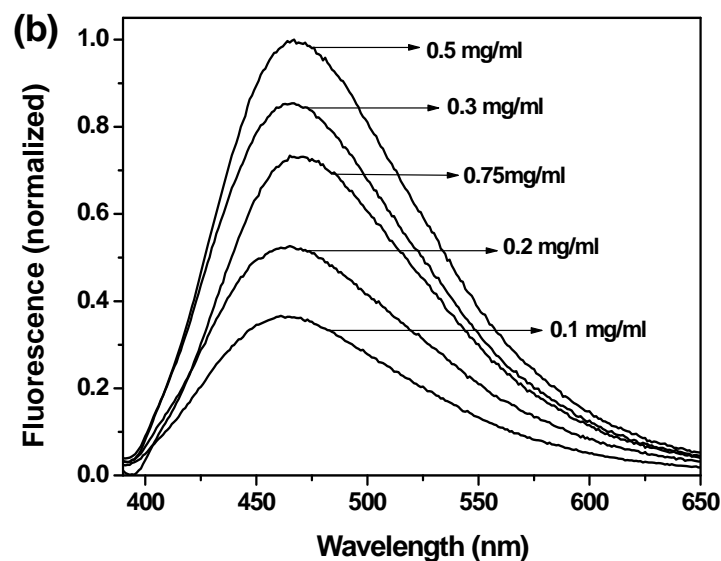
The solution behavior of the modified polymers after methylation was also studied by measuring the surface tension (Figure 2.14). The surface tension of the modified PK50 with 2-DAEA, 2-DEAEA, and 4-PcA after methylation decreases in a less dramatic manner to a limited value around 65-67 mN/m with an increase in polymer concentration. This may be explained by the fact that the modified PK50 after the methylation has a high content of the ionized amino groups around the backbone, leading to the enhanced hydrophilicity. Thus the polymers become water-soluble cationic polyelectrolytes. This is also confirmed by the fact that there are no small aggregates formed even at the high polymer concentration (10 mg/ml) by the DLS studies. It is worth to note that the observed difference in surface activity for the modified PK30 and PK50 with 4-PcA might be due to the increasing of the di-amine conversion from the 77% to 99% and to the different molecular weight of the polyketones. Indeed, we already showed and discussed above (Figure 2.12) how the protonation level (i.e. the hydrophilicity of the polymers) negatively affects the surface activity. In the present case one might notice that higher conversion for 4-PcA (as in the case of the reaction with PK50 compared with PK30) results in a stronger hydrophilic character of the polyamines (simply more hydrophilic groups are grafted along the backbone) and thus a lower surface activity, in agreement with the concept expressed above.



**Figure 2.14** Surface activity measurements for water dispersion of PK50 modified with 2-DAEA, 2-DEAEA, 4-PcA and PK30 modified 4-PcA.

All synthesized polymers behaved like intrinsically photo-luminescent materials and displayed fluorescent properties, which can be attributed to the multiple aromatic pyrrole rings in the backbone. For example, the fluorescent spectra of PK30 modified with 1,2-DAP at 100% protonation level and with 4-PcA after methylation are shown in Figure 2.15. In aqueous solution, the fluorescence spectra show maxima at around 420-430 nm for the PK30 with 1,2-DAP and around 470 nm for the PK30 with 4-PcA. A small red shift of the fluorescence emission for PK30 with 1,2-DAP takes place with an increase of concentration. The different maximum emission wavelength between these two polyamines can be attributed to their different chemical structure. The fluorescence intensity increases with increasing the initial polymer concentrations. After reaching the maximum, the fluorescence intensity decreases with further increasing the concentration. This behavior is most probably due to a self-quenching effect.<sup>21</sup>





**Figure 2.15** Normalized fluorescence intensity of (a) PK30 modified with 1,2-DAP; (b) PK30 modified with 4-PcA in water at a function of concentration.

The aqueous properties described above are very interesting when considering the possible applications of the synthesized polyamines. Their surface activity strongly suggest the application as polymeric surfactants (e.g. in the dispersion of virgin polyketones in water, see Chapter 3). Moreover, the simple presence of ammonium groups, whose amount is easily tunable by controlling the protonation reaction, suggests the use of these cationic polymers in the formation of complexes with polyanions (e.g. DNA, polyacrylic acid).

## 2.4 Conclusions

A series of new polymeric amines were prepared by chemical modifications of low molecular weight alternating polyketones with different kinds of di-amines. It was found that reaction conversion strongly depends on the steric hindrance displayed by the reactants. During the reaction, around 70-80% of the polyketones carbonyl groups could be converted into pyrrole units along the backbone. It is demonstrated that the resulting polymers, after protonation or alkylation of the amino groups, display interesting aqueous solution behavior and they could act as polymeric surfactants or polyelectrolytes. Furthermore, they exhibit fluorescence in aqueous solution, which may be promising for the use as water-soluble fluorescence probes.

## 2.5 References

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